Discrepancy between Monte-Carlo Results and Analytic Values for the Average Excluded Volume of Rectangular Prisms

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We perform Monte Carlo simulations to determine the average excluded volume $\langle V_{\rm ex}\rangle$ of randomly oriented rectangular prisms, randomly oriented ellipsoids and randomly oriented capped cylinders in 3-D. There is agreement between the analytically obtained $\langle V_{\rm ex}\rangle$ and the results of simulations for randomly oriented ellipsoids and randomly oriented capped cylinders. However, we find that the $\langle V_{\rm ex}\rangle$ for randomly oriented prisms obtained from the simulations differs from the analytically obtained results. In particular, for cubes, the percentage difference is 3.92, far exceeding the bounds of statistical error in our simulation. **Added in Revision 2: We recently found the cause of the discrepancy between the simulation result and the analytic value of the excluded volume to be the effect of an error in our simulation code. Upon rectification of the simulation code, the simulation yields 11.00 ± 0.002 as the excluded volume of a pair of randomly oriented cubes of unit volume. The simulation also yields results as predicted by the analytic formula for all other cases of rectangular prisms that we study.**

The concept of excluded volume is used widely in the statistical mechanics of gases as well as polymer systems. The excluded volume of an object is defined as the volume around an object into which the center of another similar object is not allowed to enter if overlapping of the two objects is to be avoided [1]. In the case of objects that are allowed random orientations in a specified angular interval one defines an average excluded volume $\langle V_{\rm ex}\rangle$ that is the excluded volume averaged over all possible orientational configurations of the two objects.

The excluded volume arises in the leading order concentration expansion ("virial expansion") for the pressure in the case of gases that repel each other with a hard-core volume exclusion [2]. In polymer systems, the concept arises due to the fact that in dilute polymer solutions, each polymer molecule tends to exclude all others from the volume that it occupies [3]. In studying continuum percolation with a system of soft-core objects, one of the properties of interest is the connectivity of the percolating cluster. The mean number of intersections per object is a convenient measure of the connectivity and is given by the number of object centers located within the average excluded volume of an object. Hence, the product of the critical concentration N_c of objects at the percolation threshold and the average excluded volume $\langle V_{\rm ex}\rangle$ gives the critical average number of intersections per object B_c [4–6]

$$B_c = N_c\langle V_{\rm ex}\rangle. \tag{1}$$

The behavior of B_c has been the focus of previous literature [4–6] and we recently found this quantity to be approximately invariant for systems of a given object shape independent of orientational constraints in 2-D [7]. In this paper we discuss our simulation results for the $\langle V_{\rm ex}\rangle$ of rectangular prisms, ellipsoids of revolution and capped cylinders. We find a statistically significant difference between our simulation results and the analytically predicted values for the $\langle V_{\rm ex}\rangle$ of rectangular prisms while obtaining an agreement, within statistical error, for the case of ellipsoids and capped cylinders.

In order to find the average excluded volume for a given object shape we employ a Monte Carlo simulation algorithm similar to the one used in Ref. [2]. An object of the shape under consideration is placed with its center coinciding with the center of a box of side L . The box volume is chosen to be larger than the excluded volume, but small enough to minimize the number of wasted trials. The orientation of the object is specified by the three Euler angles: $0 \le \phi \le 2\pi$, $0 \le \theta \le \pi$, $0 \le \psi \le 2\pi$. The object is given an initial orientation that is random. In order to achieve random isotropic orientations, the first and last Euler angle are drawn from a uniform random distribution while the second Euler angle is drawn from a cosine distribution. A second identical object is then introduced into the box with its center randomly positioned in the box and given a random orientation. We then determine if the two objects intersect. We repeat this procedure for $N_T = 10^9$ trials and record the number of times N_I the two objects intersect. The probability that the two objects intersect, P_I, is N_I/N_T. The average excluded volume for a pair of objects oriented randomly is $P_I L^3$, where L^3 is the volume of the box. We carry out the simulation for rectangular prisms and ellipsoids of different aspect ratios, as well as for capped cylinders. The method we use to determine the intersection of rectangular prisms is described in detail in Ref. [8]. We determine the intersection of ellipsoids using a contact function [9], and the algorithm to check the intersection of two capped

cylinders is in Ref. [10]

The analytic expression for the average excluded volume for a pair of convex bodies labeled A and B is [11]

$$\langle V_{\rm ex}\rangle = (V_A + V_B + (M_A S_B)/4\pi + (M_B S_A)/4\pi), \quad (2)$$

where V, S and M denote the volume, surface area and the total mean curvature of the two bodies respectively.

For two identical convex bodies $\langle V_{\rm ex}\rangle = 2(V + (MS)/4\pi)$. Reference [11] contains a derivation of Eq. (2) as well as the expressions for V, M and S for different shapes. For a rectangular prism with sides l_1, l_2, l_3,

$$M = \pi(l_1 + l_2 + l_3). \quad (3)$$

The analytic expression for $\langle V_{\rm ex}\rangle$ can also be obtained using a well known result in geometric probability known as the "principal kinematic formula" [12–14]. The formula gives the measure of the set of positions of the center of one object for which it intersects another fixed object which, apart from a normalization factor, is Eq. (2).

Table I contains our simulation results for $\langle V_{\rm ex}\rangle$ for a pair of identical rectangular prisms compared with the analytically obtained $\langle V_{\rm ex}\rangle$ for different aspect ratios of the prisms. The simulation results do not agree with the expected analytic values, e.g., the simulation result exceeds the analytic result for cubes by 3.92%. We see that the percentage difference decreases as the length of one side becomes much greater than the other two (i.e., as the prism approaches a widthless stick), while the percentage difference increases when the length of one side becomes smaller than the other two (i.e., as the prism tends to a platelet). Simulations for soft core rectangular prisms have also been performed in Ref. [15]. The value of $\langle V_{\rm ex}\rangle$ for cubes quoted in Ref. [15] is 10.56, in good agreement with our simulation result although the authors of Ref. [15] were unaware of the discrepancy with the analytically obtained value of 11 .

We reproduced the results earlier derived by Garboczi *et. al.* [2] for the average excluded volume of two identical ellipsoids of revolution, for different aspect ratios. Table II shows our simulation results for $\langle V_{\rm ex}\rangle$ of ellipsoids of revolution of different aspect ratios compared with the analytically obtained $\langle V_{\rm ex}\rangle$ [2]. As found in Ref. [2], we see that the simulation results for both prolate and oblate ellipsoids agree with the analytic results, to within statistical error. This is in contrast to the case of rectangular prisms.

Our simulation results for the $\langle V_{\rm ex}\rangle$ of capped cylinders compare well, within statistical error, with the analytically-obtained values for these objects [4]. The capped cylinders in our simulation consist of a cylinder of length $L = 1.0$ whose ends have hemispherical caps of radius $R = 0.25$. Our simulation results yield $\langle V_{\rm ex}\rangle = 2.8797 \pm 0.0006$ while the analytically determined value is 2.8798. The procedure in Ref. [4] to determine $\langle V_{\rm ex}\rangle$ of two capped cylinders consists of finding the excluded volume for a given relative orientation between the two, and then calculating the average value of the expression over all possible orientations of both objects. We verify that the analytic result in Ref. [4] can also be obtained using Eq. (2).

Finally we performed a simulation to determine the $< V_{ex} >$ of a sphere and a cube. Our simulation result agrees with the value obtained analytically: for a cube and a sphere, both of unit volume, the excluded volume using Eq.(2) is 9.349 while the simulation yields 9.347 ± 0.001. The analytical result for this case can be determined using the method employed in Ref. [4] and we find exactly the same result as the one obtained using Eq. (2).

We have not determined the cause of the difference between the simulation results and the analytic results for $< V_{ex} >$ of rectangular prisms. We have, however, carried out checks to try to eliminate the the possibility of certain sources of error in our simulations. Possible sources of error in the simulation are :

(i) The simulation does not generate random isotropic orientations of the objects.

(ii) The algorithm used to determine the intersection of the rectangular prisms fails to do so accurately.

(iii) The number of trials in the simulation is insufficient to obtain good statistics.

Possibility (i) appears to be ruled out by the agreement, within statistical error, of the results of our simulation for ellipsoids and capped cylinders and their analytically-predicted values. As a check on the intersection algorithm, we carry out a simulation to determine the $\langle V_{\rm ex}\rangle$ for parallel aligned cubes which yields a value of 8.000 ± 0.002 , in good agreement with the expected value of 8 [4]. We also determine the excluded volume for a number of fixed relative orientations of the prisms and confirm agreement with the corresponding analytic results. Therefore possibility (ii) also appears to be eliminated. As far as possibility (iii) is concerned, we find that there is no significant change in the value $< V_{ex} >$ after about 10^7 trials and we, therefore, believe that 10^9 trials yield good statistics. There are instances where Monte Carlo simulations yield results different from those obtained by exact enumeration, such as in the study of self-avoiding walks in percolation [16], where failure to sample certain configurations has an inordinately strong effect on the final result. However, we cannot identify any such configurations in our study of $< V_{ex} >$.

There may also be other sources of error, which we have not considered. However, with regard to this, we point out that both our simulation result for the $< V_{ex} >$ of cubes as well as the simulation result in Ref. [15] are in excellent agreement and were obtained independently and without knowledge of each other's work at the time.

Looking at our results, we observe that there is agreement between the simulation and analytic results for the $< V_{ex} >$ of ellipsoids which are non-singular objects (smooth) and have only a single point of contact

when touching externally. We find agreement in the case of capped cylinders which are non-singular objects, but which can have multiple points of contact when touching externally. Also, in the case of the sphere and cube we obtain good agreement between simulation and analytic results. In this case only one of the objects viz. the cube is singular. In the case of two rectangular prisms for which we find the discrepancy, both the objects are singular. Hence, an initial conjecture as to the cause of the difference could be the possibility that Eq.(2) does not hold for a pair of convex bodies, both of which have singular surface points. Eq.(2) is derived in Ref. [11] beginning with the assumption that the objects under consideration are non-singular and have a single point of contact when they touch externally. Thus, the derivation should not apply for objects such as rectangular prisms. After Eq. (2) is obtained, the assumption of smoothness is dropped with minimal explanation and Eq.(2) is applied to singular objects such as rectangular prisms [11].

On the other hand, the principal kinematic formula is widely accepted to be true and the literature on the subject [12–14] states that the expression must work for *all* convex bodies. Furthermore, derivations of the principal kinematic formula seem not to make any assumptions about the smoothness of the bodies under consideration.

The difference of our Monte-Carlo results from the analytically predicted values is intriguing and because of the broad applications of the concept of excluded volume, the problem merits further study.

EPILOGUE

We recently found the cause of the discrepancy between the simulation result and the analytic value of the excluded volume to be the effect of an error in our simulation code. Upon rectification of the simulation code, the simulation yields 11.00 ± 0.002 **as the excluded volume of a pair of randomly oriented cubes of unit volume. The simulation also yields results as predicted by the analytic formula for all other cases of rectangular prisms that we study.**

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TABLE I. Comparison of simulation results with analytic results for the average excluded volume of rectangular prisms of unit volume. The sides of the prisms are l_1,l_2 and l_3 with $l_2 = l_3$. The aspect ratio of the prism is defined as l_1/l_2. We estimate the uncertainty in $\langle V_{\rm ex} \rangle$ as follows: The reciprocal of the square root of the number of Monte Carlo trials yielding intersection of the two objects is the fractional uncertainty in the determination of $\langle V_{\rm ex} \rangle$. The product of the fractional uncertainty and the estimated value of $\langle V_{\rm ex} \rangle$ is the uncertainty in that value.

Aspect Ratio	Monte Carlo	Calculated	Absolute Difference	Percentage Difference
Platelets				
0.000001	1751600.0 ± 467.911	2000002.000	248402.0	12.420
0.01	182.760 ± 0.048	207.020	24.260	11.718
0.5	11.488 ± 0.002	12.000	0.513	4.272
0.6	11.058 ± 0.002	11.533	0.475	4.118
0.7	10.804 ± 0.001	11.257	0.453	4.027
0.8	10.659 ± 0.001	11.100	0.441	3.975
0.9	10.591 ± 0.001	11.022	0.431	3.911
Cube				
1	10.569 ± 0.001	11.0	0.431	3.918
Prisms				
2	11.543 ± 0.003	12.0	0.477	3.811
4	15.023 ± 0.003	15.500	0.477	3.077
8	22.774 ± 0.007	23.250	0.476	2.047
16	38.654 ± 0.016	39.1250	0.471	1.204
32	70.624 ± 0.046	39.12500	0.439	0.617
64	134.599 ± 0.175	135.03125	0.432	0.320

TABLE II. Comparison of simulation results with analytic results for the average excluded volume of randomly oriented unit volume oblate and prolate ellipsoids of revolution. The lengths of the axes of the ellispoids are a,b and c, with $b = c$. The aspect ratio of the ellipsoid is defined as a/b. The uncertainty in $\langle V_{\mathrm{ex}} \rangle$ is estimated as in Table I.

Aspect Ratio	$\langle V_{\mathrm{ex}} \rangle$ (Monte Carlo)	$\langle V_{\mathrm{ex}} \rangle$ (Analytic result)
Oblate		
0.03125	77.739 ± 0.006	77.741
0.0625	40.281 ± 0.003	40.281
0.125	21.811 ± 0.002	21.810
0.25	12.956 ± 0.001	12.956
0.5	9.077 ± 0.007	9.077
Sphere		
1	8.001 ± 0.002	8.0
Prolate		
2	9.077 ± 0.001	9.077
4	12.957 ± 0.002	12.956
8	21.813 ± 0.005	21.810
16	40.28 ± 0.014	40.281
32	77.70 ± 0.04	77.741